PREPARATION OF A DRY PRODUCT FROM CONDENSED MENHADEN SOLUBLES

RESEARCH REPORT 45

FISH AND WILDLIFE SERVICE

UNITED STATES DEPARTMENT OF THE INTERIOR

A stable, free-flowing dried soluble could be included in mixed farm-animal feeds by many manufacturers who do not have the equipment to use the condensed solubles containing 50-percent solids. Dried solubles were prepared by means of a small drum dryer from 32 samples of typical condensed menhaden solubles obtained from plants along the coasts of the Middle and South Atlantic and the Gulf of Mexico. About three-fifths of all the samples tested were readily dried and gave dry products that would be satisfactory if handled and packaged so as to prevent absorption of atmospheric moisture.

A number of chemical and physical properties were determined both for the condensed solubles and for the resultant dry products. Ten properties, or drying characteristics, for the solubles or the dried product were used to calculate a "Suitability Factor" that would permit estimating the value of a particular sample of condensed solubles to produce a satisfactory dry product. The correlation of certain properties of the condensed solubles to characteristics of the related dry products will be presented in a later report.

Improvements in certain drying characteristics were obtained with some difficult-to-dry samples of condensed solubles by the use of small amounts of additives. However, when added in amounts of 10 percent or less, none of the additives entirely prevented such features as excessive hygroscopicity, hot-plasticity, oil separation, and drum adhesion, which result in an unsatisfactory dry product.

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By C. F. LEE

Chemical Engineer, Fishery Technological Laboratory, College Park, Md.

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Fish and Wildlife Service
John L. Farley, *Director*

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Fred A. Seaton, *Secretary*

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PREPARATION OF A DRY PRODUCT FROM CONDENSED MENHADEN SOLUBLES

The problems involved in the preparation of a dry product from condensed menhaden solubles have been under study at the Fish and Wildlife Service's Fishery Technological Laboratory at College Park, Md., since August 1951. Research has not been continous; very little laboratory work has been done since June 1954. Until a pilot-plant dryer was available in February 1953, the only dry products that could be prepared were mixtures of condensed solubles with fish meal or scrap in proportions that could be dried in open pans in a steam drying oven.

The investigation of the physical constants and chemical composition of condensed solubles was expanded each year. Variability in the commercial samples and the need for more information concerning their chemical composition became more apparent as the number of samples taken was increased. Complete information regarding the samples collected in the first two seasons was not obtained, owing to the inadequacy of standard methods when applied to the analysis of condensed solubles.

After a small double-drum dryer was obtained in February 1953, the major emphasis of the project was on the preparation of pure dry solubles and the study of their characteristics. Virtually all of the samples collected in 1952 and 1953 were dried without additives in order to determine the effect on the dry products of the normal variability of composition of condensed solubles produced by different commercial plants. Finally, a more limited study was made of the effect of various additives on behavior during drying, as well as on the dry product itself.

PREVIOUS INVESTIGATIONS

The menhaden condensed solubles industry is, for the most part, of quite recent origin, having increased from 3 or 4 plants before 1950 to 24 or 25 plants in 1955. This rapid growth has permitted little time for in-plant study of processing variables and their effect on the product. Not only is operation of an expensive unit at the maximum level good business practice, but state and city regulations against water pollution are becoming more general and more strictly

enforced each year. Consequently, the stickwater cannot be discharged to waste as it was in the past. The present investigation, concerned with producing a dry product from menhaden condensed solubles, was in a sense putting the cart before the horse, but unavoidably so, because at the time the work was started there was no information to suggest that variability in the composition of solubles of the magnitude found during this investigation was present in commercial samples. The need for pilot-plant exploration of a number of the variables in the processing and handling of menhaden condensed solubles has been an incidental and unexpected development from the analytical studies on the raw material for dried solubles.

At the present time it is very difficult to recommend processing procedures that will produce fresh, homogeneous condensed menhaden solubles of uniform viscosity. Either in-plant studies or extensive pilot-plant studies with commercial-type evaporators will be necessary to supply this information. Norwegian investigators have been working with such equipment for a number of years and have solved some of the processing problems related to production of herring solubles. Unfortunately, conditions in Norway and in the United States are very different. The species of fish, the type of plant equipment, and the way the fish are handled differ, in part because air and water temperatures are much lower in Norway than in the areas where menhaden are caught. Consequently, few of the conclusions derived from Norwegian data can safely be transposed to apply to the problems of the condensed menhaden solubles industry.

There has been some pilot-plant-scale research in western Canada on solubles production, but herring was used instead of menhaden, and conditions in general more nearly resemble those in Norway. So far as is known, there has been no research specifically concerned with the production of menhaden condensed solubles, and the Fishery Technological Laboratory at College Park, Md., serving the States of the South Atlantic and Gulf Coasts, does not have the pilot-size, commercial-type evaporators needed for work of this type.

The advantages of fish solubles in a dry and easily handled form are many and obvious. Dry solubles would be far easier to store, to transport, and to use then the usual 50-percent solids product now marketed. The appearance and texture of solubles vary considerably. Condensed solubles have been observed that were semisolids even at summer air temperature, and at least half of the samples examined were virtual solids at temperatures below 35° to 40° F. This viscous material is difficult to mix with the other ingredients in mixed feeds, requiring the use of special equipment not commonly found in the smaller feed mills. The more fluid samples showed a disposition to separate into two or more liquid phases, and in some instances a solid phase also settles out during storage at 40° F. On prolonged storage, colorless crystals have been frequently observed, sometimes in considerable

quantity, as an additional type of nonhomogeneity.

Efforts to produce solubles in dry form have been fairly numerous. Almost all of this work has been carried out by industrial laboratories, and, unfortunately, the results of the work have not been published. However, as of 1951—and the situation is not believed to have altered greatly since that time—no process had been developed that would prepare an entirely satisfactory dry product from random, unselected lots of condensed fish solubles.

At this point, an important distinction must be made between essentially pure, 100-percent dry solubles, and products in which condensed solubles are mixed with fish meal or other absorbents. The mixtures usually carry only relatively small proportions of solubles, and they dry without difficulty. No doubt the products of this type that are produced in greatest bulk are the "full" meals or "whole" meals. These are mixtures in which fresh press cake, or dried or partially dried scrap, is the absorbent for condensed solubles in approximately the same proportion as that in which soluble solids were present in the whole cooked fish. The amount of solubles solids present in these whole meals may vary considerably, and the amount is difficult to determine exactly because of the similarity in proximate composition to the absorbent meal. A method for estimating the solubles added to whole meals or more concentrated mixtures of meal and solubles has been proposed by Lee (1954). No data are available now, either in this country or in foreign countries, on the quantity of whole meals being produced. Extensive research has been conducted in Norway on this type of product, and the producers there are believed to be using almost all of the solubles in this way. The South African pilchard-meal industry has installed evaporator plants to concentrate stickwater for use in whole meals if a demand for this product arises. For the most part, in the United States this operation is limited now to filling special orders, or to absorbing surplus stocks of solubles during periods of glut production.

In foreign countries, condensed solubles are used primarily in the manufacture of whole meals because the limited native demand for solubles necessitates the export of most of the production. In exporting whole meal, shipping charges are saved because water, approximately equal in weight to the added solubles solids, is driven off in drying the meal-solubles mixture. The dry meals are also easier to handle, store, and ship. The sale price of condensed solubles was 3¾ to 4 cents a pound during most of the 1955 season. If the solids added to whole meals by condensed solubles are assumed to be of the same value as the original meal, this is equivalent to 3¾ cents a pound of solubles on the basis of a meal price of $150 a ton. Therefore, at virtually the same price in either form, the advantages of the whole meal are weighed against only the added cost of mixing and redrying the meal-solubles mixture.

Mixtures of fish solubles with other fillers or carriers, such as dry

yeast, soybean meal, bran, alfalfa meal, and whale solubles, have been, or are now, produced in limited quantities. It is believed, however, that about 90 percent of the United States production of condensed solubles, which has totaled more than 150 million pounds a year for 1954 and 1955, is marketed in the wet, or 50-percent solids, form.

PREPARATION AND STUDY OF SOLUBLES-MEALS MIXTURES

From its initiation, the object of this project has been to prepare pure dry solubles, or, failing this, to prepare a dry mixture consisting mostly of solubles solids with minimum levels of additives.

As previously indicated, a drum dryer was not available in 1951, and trials showed that no appreciable amount of dry solubles could be prepared in a drying oven. Only a very thin layer could be dried in this way without forming a tough coating which greatly hindered further drying. Further experimentation before obtaining the drum dryer was limited to the preparation and study of mixtures of condensed solubles with fish meal or scrap. This work will be mentioned but briefly, because the equipment available and the methods used did not closely approximate commercial practice.

To obtain a dry product that would be not only a whole meal but also a solubles carrier or concentrate, an effort was made to determine the amount of condensed solubles that fish meal or scrap could absorb and still result in a mixture that would dry readily and yield a reasonably nonhygroscopic product.

Condensed solubles were added to the meal or scrap sample in the bowl of a motor-driven paddle-type mixer until the mixture began to ball up in a sticky mass. The mixture was dried overnight in a flat pan in a steam oven; it was then ground, and more solubles were added to again produce about the same consistency. This process was repeated until four lots of solubles had been added. The amount of condensed solubles added to each stage amounted to 20 to 30 percent, by weight, of the dry material. The total solubles solids thus added in four stages amounted to approximately one-third of the total solids in the final dry mixtures.

In a second, and similar, series, considerably more solubles were added at each stage to produce an almost soupy initial mixture, which was judged to be much too wet to be handled in the standard rotary meal dryer. In this series, condensed solubles equal to 35 to 55 percent of the weight of dry material was added at each stage. The equivalent amount of solubles solids added in these stages was 66 to 85 percent of the original base material, or 40 to 46 percent of the total solids of the final dried mixtures.

All of these mixtures dried fairly readily when held in a steam oven at 160° to 175° F. for several days, and the lumps were friable and could be ground with little difficulty. The

ground material, although dustier than an ordinary fish meal, did not show an unusual tendency to pick up moisture at the conditions of temperature and humidity prevailing in this laboratory during October and November.

Attempts to determine the amount of water absorbed under controlled conditions of higher relative humidity gave reasonably consistent results. These conditions of controlled relative humidity were obtained through application of the principle that a saturated solution of certain salts containing an excess of solid phase will maintain a definite and constant relative humidity in an adjacent confined air space at any given temperature. Originally, four aquariums of different dimensions were used. The saturated salt solution was held in an evaporating dish at one end of the bottom, and the 18- to 20-g. (gram) portions of the meal mixtures were placed in smaller evaporating dishes on the same level.

The salts used were sodium carbonate, ammonium sulfate, sodium nitrite, and magnesium nitrate, which gave relative humidities of approximately 87, 81, 66, and 52 percent, respectively. Trial showed that equilibrium was reached very slowly, or not at all, with this arrangement, because the sample size was too great, the proportion of volume of air space to surface area of the controlling solution was excessive, and the test dishes were not sufficiently close to the salt solution in the aquariums.

Later, this technique and the equipment used to determine water absorption were modified. The solutions were changed to include a lower humidity range, and much smaller samples and chambers were used. This procedure, described in detail in the paragraph on "Moisture absorbed in humidity chambers" (p. 10), was the one used routinely for comparing the hygroscopic characteristics of all the drum-dried solubles, both with and without additives.

METHODS OF PREPARING DRY SOLUBLES

There are several ways in which the water content of condensed solubles can be reduced to give a dry product. One method is spray drying, which has been tried with some success on a laboratory or experimental scale. The fish-meal industry, however, is characterized by extreme fluctuations in catch. It is not uncommon for 1,000 tons of raw fish to be landed at a single plant in a few hours. This amount of fish would produce an estimated 150,000 gallons of stickwater (1,200,000 pounds). If the stickwater contains an average of 6-percent solids, this amount (1,200,000 pounds) would yield almost 150,000 pounds of condensed solubles (50-percent solids) per day. Heavy production on this scale may continue for a week or more and may be followed by periods of very light catches; consequently, it is very difficult to determine the most practical size of a costly spray-dry unit. The excessive variability in viscosity of condensed solubles has com-

plicated experimental spray drying by making it difficult to get consistent performance from the device that atomizes or disperses the solubles into the air streams. In some instances, particles may coalesce and coat the sides of the chamber.

Methods involving azeotropic drying can also be used to produce dry solubles, but, again, fixed cost of equipment large enough to take care of peak production is high, a large solvent inventory is necessary, and constant care is necessary to avoid solvent losses. These losses may result from leakage or from carry-over of solvent in the dried product. Solvent loss may not only reduce or eliminate the profit margin, but may also lead to toxic hazards of solvent in the air or in the product or to a fire hazard, depending upon the particular solvent used. Dichloroethylene, and hexane are some of the solvents that have been used commercially in the azeotropic-drying process. Limited experimentation in drying solubles by this process indicates that the problem of solvent carry-over in the dried material may be greater than for most products. Normally, direct steam is used to remove the last traces of solvent. This process must be short and very carefully controlled with dry solubles because the product has a great tendency to absorb moisture.

There are indications that a few of the vitamins of the vitamin B complex may be partially soluble in certain solvents, which may lead to losses in excess of those resulting from the heat-drying processes. Since these vitamins are important nutrients supplied by fish solubles, the possibility of losses from this source should be considered in the use of the azeotropic method for drying solubles.

Drum dryers have the advantage of relatively low cost for large drying capacity, as well as ease of control of drying effectiveness at any stage of the process through simple adjustment of roll speed, drum-surface temperature, or rate of feed.

DRYING CHARACTERISTICS OF DRUM-DRIED SOLUBLES

The drum dryer used in these studies was a small laboratory model with double drums 6 inches in diameter by 6 inches in length. Roll speed could be positively controlled, forward or reverse, between 0 and 12 r. p. m. (revolutions per minute), through a variable-speed transmission. A reducing valve permitted adjustment of the steam pressure in the drum from 20 to 85 pounds per square inch, which was equivalent to a temperature range of approximately 260° to 325° F. One of the drums was mounted on a horizontal slide so that its position could be controlled by a hand screw at each end, to a space of from 0 to about ¼ inch between the drums.

A few trials quickly showed that it was almost impossible to produce a dry product with the lower range of steam pressure; without exception, it was necessary to use the 60 to 75 pounds per square inch range (308° to 321° F.). Drum speed, which controlled the time of ex-

posure to the heating surfaces, could not be increased beyond 1 r. p. m. for satisfactory results. Generally speaking, the drums were operated at 0.5 r. p. m. to obtain a dry product, and for some samples that were hard to dry, the drum speed was reduced to 0.2 r. p. m. On a commercial-size drum of larger diameter the same drying effect would be obtained with a greater drum speed.

For most of the samples, a spacing of 0.006 inch to 0.009 inch between the drums gave a suitable film thickness, but this space could be increased slightly for samples of higher viscosity.

The problem of rate of feed to the drums was readily solved by maintaining an excess of wet solubles in the "pinch" between the drums, confined by the end plates. This pool of solubles fed the preheated material smoothly and evenly over the drums and resulted in considerable preliminary concentration which was of particular value for the samples of lower solids content. The way in which the wet material is fed to the drums, and the way in which the dry solubles are removed from the drums by the knives, are shown in figures 1 and 2.

Sample differences that developed during drying

A number of differences between the samples of condensed solubles became apparent during the drying operation. Initially, the behavior and appearance during drying of each sample were recorded in descriptive terms. As work progressed, the need for numerical rating of characteristics became apparent.

Eventually, seven characteristics were selected as being responsible for the major differences in appearance and behavior of samples during the drying process. Numerical ratings of 1 to 10 were given each characteristic, a rating of 1 being the desired condition. Subsequently, the dried material was ground, and the powder was rated in the same way on three additional characteristics. The ratings on the 10 characteristics were used to develop a "Suitability Factor", as described in the following section. The 10 characteristics, their significance, and the conditions corresponding roughly to the variation encountered for each (see table 1) are as follows:

1. *Oil separation.*—When the solubles were heated between the drums, the emulsion, which for some samples kept considerable amounts of oil in colloidal suspension, was broken with a resulting separation of oil. There was no oil separation from samples containing less than 5 percent oil. At the other extreme, considerable oil collected on the surface of the concentrated material between the drums and wet the dry solubles so that the last part of such lots had to be discarded.

2. *Hot plasticity.*—The tendency of some samples to remain plastic and sticky on the hot drum which is called hot plasticity, varied markedly. A small number of samples were flaky and friable on the drums and were removed by the knife edge as a thin crumbly sheet.

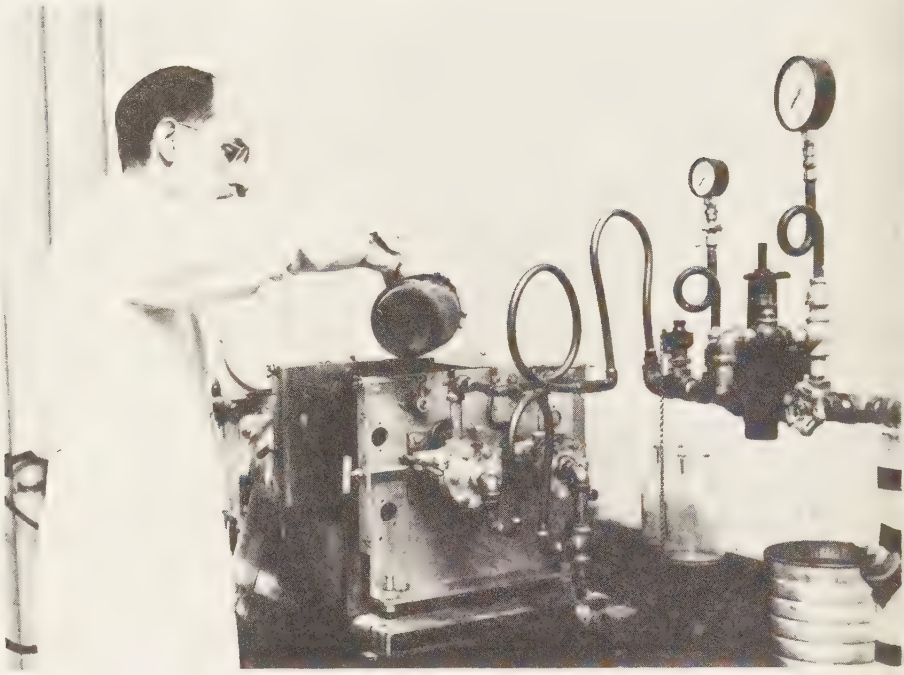

Figure 1.—Adding menhaden solubles to drum drier for preparation of dry solubles.

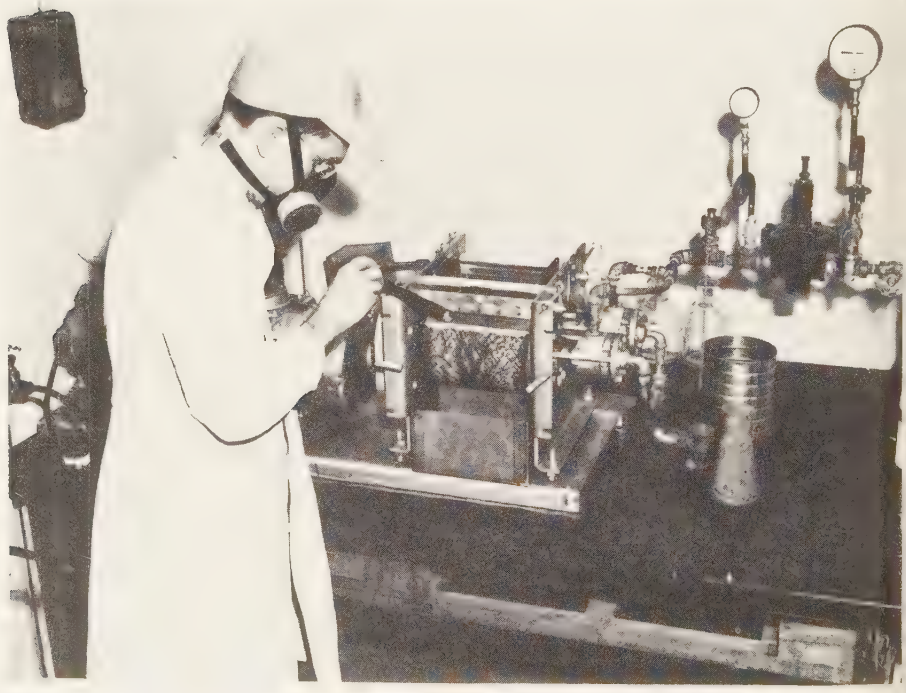

Figure 2.—Producing dry menhaden solubles on pilot-plant drum drier.

Code identification of sample [1]	Type [2]	Date collected	Condensed menhaden solubles													Pure dried solubles											
			Dry solids	Crude protein	Ammonia	Corrected protein [3]	Fat	Total ash	Water-insoluble matter	Water-insoluble ash	pH	Refractive index	Specific gravity	Viscosity	Thixotropy	Suitability Factor	Oil separation [4]	Plasticity [4]		Color [4]		Drum adherence [4]	Homogeneity [4]	Vapor odor [4]	Moisture absorption in humidity chambers [4]	Texture after humidity test [4]
																		Hot	Cold	Original	Ground					
			Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*				*Degrees*	*Rating*	*Percent*										
NA1	S	8/53	49.2	33.1	0.38	31.2	6.1	8.4	5.6	0.11	4.82	1.4232	1.189	106	2+	27.8	20	21	8	6	8	10	1	6	32	28
NA2	P	8/53	47.8	32.5	0.73	28.8	6.5	10.4	3.3	0.11	5.32	1.4220	1.190	56	------	31.1	15	21	12	4	6	6	3	1	32	35
NA3	S	8/53	53.5	33.5	0.88	28.9	10.8	9.4	6.6	0.20	4.60	1.427	1.196	157	4−	34.7	35	28	16	12	8	2	1	12	16	35
NA4	P	8/53	52.5	37.1	0.39	35.1	8.3	7.7	3.8	0.29	[5] 5.93	1.4322	1.184	775	------	39.4	30	35	16	6	6	14	7	12	28	28
NA5	P	10/53	48.6	32.2	0.28	30.7	5.3	8.5	5.6	0.22	[5] 5.81	1.423	1.195	3,000	------	28.1	5	21	4	10	10	20	4	6	40	21
SA1	S	10/52	49.7	33.6	1.03	28.3	6.5	9.6	3.7	0.18	4.71	1.4269	1.201	31	------	55.6	5	56	28	14	10	2	1	36	32	56
SA2	S	10/52	47.2	31.4	1.14	25.5	8.6	9.2	4.4	0.42	5.24	1.4260	1.182	55	------	53.9	10	49	20	14	14	2	4	36	36	49
SA3	S	10/52	49.2	32.5	1.03	27.2	7.5	9.9	4.6	0.27	4.71	1.426	1.192	63	------	48.9	20	42	16	12	10	2	3	30	32	49
SA4	S	10/52	49.3	31.8	0.38	29.9	8.1	8.6	5.4	0.20	4.02	1.420	1.190	84	------	31.7	25	21	8	8	6	6	1	24	20	35
SA5	S	10/52	50.0	29.0	0.77	25.1	10.1	9.4	4.2	0.30	4.98	1.424	1.182	78	------	57.8	40	42	24	16	12	2	6	36	28	42
SA6	S	7/53	48.4	31.3	1.70	22.6	7.7	13.0	3.6	0.13	3.24	1.416	1.229	54	------	72.8	25	56	28	16	16	2	3	54	32	70
SA7	S	7/53	43.9	33.6	1.42	26.3	7.7	7.8	6.1	0.24	5.58	1.4248	1.161	46	------	63.6	30	56	16	18	18	2	6	42	32	49
SA8	S	7/53	52.4	32.7	0.54	30.0	11.5	8.3	5.2	0.10	4.27	1.4232	1.176	137	1+	27.5	30	21	8	4	10	2	3	18	8	35
SA9	S	7/53	53.3	36.6	1.37	29.5	7.0	11.4	4.0	0.06	4.52	1.4207	1.225	114	1+	57.5	5	63	32	16	12	2	1	36	24	56
SA10	S	9/53	48.4	31.2	1.09	25.6	8.4	9.5	3.6	0.18	4.39	1.4186	1.194	30	------	57.2	25	42	12	16	14	2	3	34	28	56
SA11	S	9/53	47.0	32.2	1.23	25.9	6.9	9.1	4.3	0.28	5.20	1.4225	1.182	41	------	42.2	15	42	12	14	10	2	1	30	24	42
SA12	S	9/53	49.1	31.1	0.44	28.8	7.1	8.0	4.9	0.18	4.16	1.4235	1.188	60	------	26.9	20	28	8	10	8	6	1	12	16	28
SA13	S	9/53	49.9	29.4	0.42	27.2	10.9	8.5	3.1	nil	4.88	1.4239	1.172	68	------	42.2	25	49	12	14	12	6	1	18	20	35
SA14	S	9/53	43.1	33.5	1.61	25.2	1.5	11.6	4.2	0.57	5.12	1.4188	1.216	183	2+	34.2	5	28	8	4	2	2	1	24	40	49
SA15	S	9/53	39.8	34.6	2.85	19.9	3.7	13.0	3.4	0.45	4.96	1.4202	1.223	54	------	49.4	15	28	12	16	14	2	1	54	20	56
SA16	S	9/53	48.8	31.8	0.50	29.2	4.9	8.4	6.2	0.36	4.43	1.4035	1.181	253	3−	18.9	5	14	4	2	4	16	1	6	28	28
SA17	S	10/53	51.8	32.7	0.42	30.5	9.7	8.5	5.1	0.22	4.07	1.419	1.190	125	2+	30.0	35	28	4	8	8	2	1	18	16	28
SA18	P	11/53	43.7	32.3	0.42	30.1	1.3	9.6	1.0	0.02	[5] 5.90	1.4201	1.206	58	------	51.4	5	56	4	4	6	[6] 60	2	6	40	42
EG1a	S	8/53	46.7	38.0	1.15	32.1	1.5	6.6	3.3	0.21	4.50	1.4248	1.201	20	------	20.5	5	35	12	2	2	2	1	12	16	28
EG1b	S	8/53	43.2	34.4	1.11	28.7	1.6	5.6	3.0	0.14	4.65	1.4150	1.178	13	------	25.3	5	42	16	4	2	2	1	12	12	35
EG1c	S	8/53	44.0	32.7	1.25	26.3	1.7	6.8	4.0	0.22	4.69	1.4188	1.189	30	------	32.8	5	63	20	6	2	2	1	12	12	35
EG2	S	8/53	47.4	34.4	0.96	29.5	7.4	5.5	7.6	0.82	[5] 5.94	1.4199	1.150	217	2+	31.9	25	14	4	12	18	2	9	18	32	21
WG1a	S	8/53	41.7	40.1	4.19	18.6	2.3	12.4	3.3	0.25	5.14	1.4252	1.253	29	------	54.4	5	56	36	12	4	2	3	42	20	56
WG1b	S	8/53	42.7	39.4	4.14	18.1	2.1	13.1	3.0	0.26	5.05	1.4218	1.262	28	------	48.6	5	49	32	10	4	2	1	36	20	56
WG2	S	8/53	49.7	35.8	1.17	29.8	8.9	7.5	9.2	0.49	4.88	1.4257	1.183	216	4−	18.6	15	14	4	14	14	2	1	24	12	7
WG2	P	8/53	44.4	30.8	1.44	23.3	11.3	9.7	5.9	1.04	[5] 6.13	1.4182	1.144	360	------	46.4	30	21	8	16	20	2	1	24	36	49
WG3	S	8/53	46.1	37.8	2.67	24.0	2.7	10.1	3.8	0.25	4.49	1.4226	1.218	203	2−	47.5	5	49	12	14	8	2	6	42	24	49
Minimum	------	------	39.8	29.0	0.28	18.1	1.3	5.5	1.0	nil	3.24	1.4035	1.144	13	------	18.6	----	----	----	----	----	----	----	----	----	----
Median	------	------	48.4	32.7	1.09	28.3	7.1	9.2	4.2	0.22	4.69	1.4225	1.190	68	------	39.4	----	----	----	----	----	----	----	----	----	----
Maximum	------	------	53.5	40.1	4.19	35.1	11.5	13.1	9.2	1.04	[5] 5.58	1.4322	1.262	3,000	------	72.8	----	----	----	----	----	----	----	----	----	----

[1] NA refers to North Atlantic including Chesapeake Bay, SA to the South Atlantic, EG to the Gulf of Mexico east of the Mississippi delta, and WG to the Gulf west of the delta. The numbers indicate different plants within each area from which samples were obtained. The letter subscripts for two Gulf plants indicate samples from tanks in which the solubles had been held for varied periods of storage.

[2] S refers to composite sample taken from storage tank; P refers to sample taken after processing and before being pumped to storage.

[3] Corrected protein is equal to the total crude protein minus the protein equivalent of the ammonia ($NH_3 \times 5.15$).

[4] The values are the product of "weight" times "rating", as described in the footnotes of table 3 in calculation of the Suitability Factor.

[5] These pH values are for nonacidulated samples, direct from evaporators and are not included in calculating the median.

[6] The drum adherence for this sample was so extreme as to make it virtually impossible to dry, so it was rated off the 1-to-10 scale used for the other samples.

For most samples, the sheet was rather soft at the drum temperature used and tended to accumulate as semiplastic folded ribbons that dropped off or could be pulled from the knife edge with little difficulty. For a few samples, the dried material was so soft that it collected on the knives in an adherent gummy roll that had to be scraped off the knife edge with a spatula (see fig. 2).

3. *Cold texture.*—Most of the samples that were "semiplastic when hot" became quite brittle when cooled to room temperature, but other samples showed a gradation down to a stage of cold plasticity bordering on tackiness.

4. *Drum adherence.*—In spite of the sticky gluey nature of semidried solubles, most of the dried samples were removed from the rolls cleanly with normal tension on the knife edges. Two or three samples, for reasons unknown, adhered to the rolls wth almost unbelievable tenacity. These samples carried under the knife edges even at the maximum tension. This characteristic was almost sufficient to classify these samples as unsuitable for drum drying, at least with the equipment available.

5. *Color.*—The color (a minor factor) of the dried material before grinding varied from a light yellow or grayish yellow (which was considered preferable) to an atypic greenish black. Most samples were brown or reddish brown when dry.

6. *Homogeneity.*—Fresh samples of condensed solubles were normally homogeneous liquids when separated liquid phases were remixed. During storage, however, almost half of the samples developed crystals, which showed on the drums as white spots in the dry sheet. The rating was based on the size and quantity of spots. Homogeneity was considered desirable, primarily because of ease in mixing, pumping, and controlling feed to the drums in a plant-scale operation.

7. *Vapors.*—Under the influence of heat, the substances causing the natural "characteristic" smell of the solubles were carried off to a large degree in the steam and vapors arising from the drums. It may not have been absolutely accurate to rate any sample "1" (best), although some were only mildly disagreeable. Others ranged up the scale to a few at the other extreme, which could be described as nauseous and noxious. The samples that were rated above 4 or 5 for this characteristic were often irritating to eyes and respiratory tract, so that it was desirable to wear a face mask with an "organic vapors" cartridge during the drying process (fig. 2).

8. *Color of ground material.*—The color of the ground solubles was sometimes lighter or darker than the dry material on the drums and was rated separately in the same way (see paragraph 5, Color).

9. *Moisture absorbed in humidity chambers.*—In most instances, the ground dry solubles were not subjected to chemical analysis, except for the determination of residual moisture. Further comparison was based on data obtained from exposure of the dry ground material in six "humidity chambers." The principle involved here is described

under the section on meal-solubles mixtures. Saturated solutions of the following salts, with an excess of the solid phase, maintained approximately these relative humidities at 70° F.: $CaCl_2.6H_2O$, 32; $Zn(NO_3)_2.6H_2O$, 42; KCNS, 47; $Na_2Cr_2O_7.2H_2O$, 52; $NaBr.2H_2O$, 58; and $NaNO_2$, 66 percent. For this determination, exactly 5 grams of the dry ground solubles were weighed into tared petri-dish tops and distributed in a thin layer over the bottom of the dish. One dish for each sample was stacked in each of the six chambers containing the humidity-controlling solutions. The dishes in the stack were separated by glass-rod triangles, and the chambers were closed with window-glass plate lids sealed airtight with petroleum jelly. No. 10 cans were used as chambers; each can would hold six samples at a time. The cans were varnished inside to prevent corrosion by the salt solution. It was found that when the chamber size (the volume of enclosed air) was limited the samples reached a condition of moisture equilibrium in 4 days. The dishes were weighed immediately, and the percentage of moisture picked up was calculated by multiplying the gain in weight, in grams, by 20.

10. *Texture after humidity test.*—At the time of weighing, the texture of samples at each level of relative humidity was noted and was given a numerical rating of 1 to 10, according to an arbitrary scale—for example, a rating of 2 indicated a sample that had a slight crust, 4 indicated a sample that formed a fairly firm cake that was not sticky but had a slight tendency to pack, and 7 indicated a sample that was slightly sticky and could be rolled into a ball with the fingers.

The data for the characteristics described in the paragraphs on "Moisture absorbed in humidity chambers" and "Texture after humidity test" were composed of six separate values, one for each level of relative humidity. The procedure used to convert these sets of values to the desired rating of 1 to 10 for each sample, is best illustrated by several samples. The data obtained by exposing 5 typical samples of dry solubles to 6 controlled relative humidities are given in table 2 (in the second column from the

Table 2.—Data derived from exposure of dried solubles in humidity chambers

Sample	At relative humidity of—						Cross totals	Rating
	32	42	47	56	58	66		
	Per-cent	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*		
No. 139:								
Moisture absorbed in humidity chambers	2.2	5.3	8.8	13.9	16.9	22.4	69.5	9
Texture after humidity test	2.0	5.0	6.5	8.0	9.5	10.0	41.0	7
No. 150:								
Moisture absorbed in humidity chambers	2.4	5.0	6.9	9.2	10.9	15.2	49.6	2
Texture after humidity test	2.0	4.0	5.5	7.5	6.5	8.5	34.0	5
No. 157:								
Moisture absorbed in humidity chambers	3.7	5.9	8.2	12.6	15.2	18.9	64.5	7
Texture after humidity test	1.5	2.0	3.0	6.0	6.5	8.0	27.0	4
No. 165:								
Moisture absorbed in humidity chambers	2.0	4.2	7.5	11.3	14.6	20.1	59.7	6
Texture after humidity test	2.0	5.0	7.5	8.5	9.0	10.0	42.0	7
No. 176:								
Moisture absorbed in humidity chambers	3.1	5.6	8.6	13.6	17.5	24.5	73.5	10
Texture after humidity test	1.5	2.0	3.0	5.0	6.0	7.5	25.0	3

right, these data have been totaled). Similar totals for all samples ranged from 49.6 to 74.6 for percentage of absorbed moisture and from 18.0 to 51.5 percent for the texture after humidity test. A single numerical rating was needed for each characteristic, but a simple average will not give the desired spread for values of 1 to 10. To obtain this spread, the range was divided into suitable intervals for each. Thus, for moisture absorbed in humidity chambers, a total of 47.0 percent or less was rated 1, and each additional interval of 3 percent increased the rating by 1 unit. For ratings of texture after humidity test, a total of 18.0 percent or less was rated 1, and each additional interval of 3.5 percent increased the rating by 1 unit. The ratings in the right-hand column of table 3 are the rating intervals in which the individual totals fell.

Suitability factor

Each sample of condensed solubles was given ten 1- to 10-scores, which, in combination, fairly accurately described its behavior during drying, its suitability for drying, the appearance of the dry product, and its reaction when exposed to the conditions of high relative humidity (previously described). However, a simple total of these individual scores did not give an accurate measure of the relative merits of any given sample, because some of the characteristics, such as color and homogeneity, were considered to be of less practical importance than others, such as hot plasticity. Each characteristic was assigned as arbitrary weight to represent its relative practical importance, assuming that the samples were to be used for the commercial production of dry solubles. By this means, the ten ratings were combined to a single weighted value called the Suitability Factor. This value theoretically could range from 0 to 100; the smaller the value the more desirable the condensed solubles were for drum drying. For the 32 samples of pure dried solubles included in this analysis for suitability, a range of values from 18.6 to 72.8 was obtained.

The precedure and method of calculating the Suitability Factor, as shown in table 3, is an example of a typical sample of condensed solubles that was dried during the tests.

Table 3.—Calculation of Suitability Factor for sample No. 172a

[Dried at 70 p. s. i. steam pressure, 0.007 in. drum space, and 0.4 r. p. m. drum speed]

Characteristic	Grade [1]	Weight [2]	Product
1. Oil separation	4	5	20
2. Hot plasticity	4	7	28
3. Cold texture	2	4	8
4. Drum adherence	3	2	6
5. Color	5	2	10
6. Homogeneity	1	1	1
7. Vapors	2	6	12
8. Color of ground material	4	2	8
9. Moisture absorbed in humidity chambers	4	4	16
10. Texture after humidity test	4	7	28
Total		40	137

[1] Grade assigned on basis of 1 to 10, low-grade values being the most desirable.

[2] Weight assigned to each characteristic to represent its relative practical importance in making a satisfactory dried product.

$$\text{Suitability factor} = \frac{[137-(40)\ (1)]\ 100}{(40)\ (10)-(40)\ (1)} = \frac{137-40}{3.6} = 26.9$$

Source of samples

In the three seasons during which samples of solubles were collected for this study, 60 samples of fish solubles were collected; 8 samples were obtained in 1951, 23 in 1952, and 29 in 1953. Most of these were commercial samples, that is, they were obtained from storage tanks at the plants. These samples have a known history as to plant and geographical location, type of equipment used in preparation, and usual processing practices for the particular plant. However, the exact date of preparation was not known, because the tanks held the composite of several days or weeks of production. For these samples, information regarding the length of trip, freshness of fish, area of fishing, solubles yield per 1,000 fish,[1] and similar variables had little significance.

In a few instances, samples were obtained directly from the evaporators, or as the hot condensed solubles were being run to storage. These samples represent a stickwater composite that covers at least 1 day's catch, because normally the stickwater is run to temporary storage and the evaporators are started up the next morning.

About half of the samples were obtained from the plants nearest to the laboratory at College Park, Md., with 24 samples from the 5 plants in the Chesapeake Bay area, and 7 samples from plants in Delaware and southern New Jersey. An additional 23 samples were collected from the South Atlantic and the Gulf of Mexico on two trips along the coast. The first of these trips was made in June 1952, and the second in late August and early September of 1953. Twenty plants are represented in this sampling, including all except two of the major plants then in operation. Two others, for which samples were not obtained, operated only a very short time during these two seasons.

Origin of variability

In regard to natural variables, the limited number of solubles samples per plant per season did not permit estimation of the significance of seasonal influence. As for biological factors, it is known that the major species of menhaden in the catch from the Gulf of Mexico differs from that of the Atlantic. Beyond this fact, little is known of the distribution of possible subspecies or how many fish populations are involved in the catch from the widely scattered areas in which the fishery is conducted. These factors may have some effect on the nature or composition of the condensed solubles, but, in general, it is believed that processing factors are of predominate importance for this product.

Basically, there are only two processes used by the menhaden industry for concentrating stickwater to make condensed fish solubles. The most common is the multistage vacuum evaporator, but several of

[1] Thousand (fish) is a unit of measure peculiar to the menhaden industry. It is, in fact, a volume measure equal to 22,000 cubic inches. The conversion factor commonly used is 1,000 fish = 667 pounds, or 3,000 fish per ton.

the smaller plants in the South use a Vincent evaporator, which is a modification of the spray dryer. For the latter equipment, the stickwater is finely dispersed into a hot-air blast in a cyclone-like chamber. Part of the moisture is carried off in the air stream, while the concentrated stick or solubles collects on the sidewalls and runs down to a sump. Some difficulty has been encountered in handling high-viscosity samples in Vincent evaporators. Consequently, autolysis is commonly encouraged in order to reduce the viscosity of the finished solubles, by holding the warm stickwater for some time before evaporation.

It is not difficult to explain differences in the solubles produced by these two processes, but it is difficult to explain how the product from different plants using the same type of equipment can show the variations that have been observed in these experiments. Such variations are not limited to interplant samples, but are found between solubles samples processed at different times by the same evaporator-plant foreman in a given plant. No attempt will be made to explain these variations. In all probability, extensive pilot-plant studies would be required to determine the effect of even a single one of the factors involved. It is generally agreed, however, that the condition of the fish at the time of processing has a great effect on the characteristics of the stickwater and of the solubles made from it.

Analytical methods

As indicated previously, it was realized almost from the first experience with condensed menhaden solubles that much additional analytical data would be needed. This type of data is not available in any of the literature on condensed menhaden solubles, and such information was necessary to explain the differences observed in the behavior of condensed solubles during the drum-drying process, and to explain differences in the dried product. Some modifications of methods and precautions in the use of standard methods were found to be essential. The procedures used will be described briefly, so far as they differ from the usual practice.

Dried solids.—This determination is complicated by the tendency of solubles to form a tough impervious coat that holds in moisture, and also by the strong attraction of solubles for moisture from the air, which possibly is due to the sulfuric acid added as a preservative to the finished condensed solubles. The method, which is similar to that used by some plant laboratories, consists in weighing 1 to 3 g. of solubles into a petri dish and adding enough water to result in a very thin film over the dish surface when the mixture is dried. Drying the sample in an air oven at 215° F. overnight, or at 260° F. for 2 to 4 hours, usually gives constant weight. It has been observed, however, that certain samples contain a substance, other than water, that is driven off in this same temperature range.

It is more difficult to determine the moisture in dried solubles than in condensed solubles. On one occasion, a group of nine samples of dried solubles in triplicate was held

over a weekend (48 hours) in an oven at 230° F., removed and weighed, then returned to the oven and held at this temperature for 4 more days, except for the short time required for daily weighing. Typical of the results obtained in this experiment are the following sets of values for (apparent) percent moisture calculated from the succession of 4 or 5 daily weights for individual sample cans: Sample 174, can 1—4.55, 7.71, 7.89, 9.24, and 10.46 percent; sample 174, can 2—3.50, 5.38, 7.68, 7.76, and 10.07 percent; sample 175, can 3—2.74, 4.14, 4.35, and 4.90 percent; and sample 172, can 1—2.45, 4.67, 4.72, and 5.01 percent. The first two sets of values are for the same sample, thus showing that the rate of loss in weight is irregular even for duplicates of a given sample.

The irregular and continuing loss is, presumably, not due to decomposition, because some of the samples that behaved in this manner remained light in color throughout the week, while others that turned almost black reached substantially constant weight in 2 or 3 days.

Crude protein.—Nitrogen is easily determined by the Kjeldahl digestion method. However, the use of the usual factor of $N \times 6.25$ to convert the percent of nitrogen to percent crude protein gave rather unusual results with some samples. The most extreme example will serve to illustrate the situation. A sample of condensed solubles with 41.7 percent total solids and 12.4 percent ash was found to have 40.1 percent crude protein. This sample was found to have nitrogen volatile with calcium hydroxide equivalent to 4.19 percent ammonia. When the crude-protein content was corrected for this nonprotein nitrogen, the corrected protein content was only 18.6 percent. This finding led to the adoption of determination of ammonia nitrogen as a regular procedure on all samples, and corrected values for protein are included in table 1.

Ammonia nitrogen.—A 1- to 3-g. sample of solubles is weighed by difference into a Kjeldahl flask, washed down with 150 ml. of distilled water, and an excess of calcium hydroxide is added. The volatile substances are distilled into boric acid and titrated in the same manner as for the total nitrogen determination, except that the distillation has to be very slow because of the great tendency to foam.

Fat.—The most practicable method found for the determination of fat in condensed solubles is the Majonnier method, or a similar procedure involving acid digestion of the protein. Condensed solubles are almost impossible to dry—even with considerable absorbent material such as asbestos or sand—so that a Soxhlet-type extraction of oil may be made. Most samples cannot be dispersed by ordinary means into a solvent phase for direct extraction of the wet material.

Ash.—The ash of condensed menhaden solubles often is fusible at the usual ashing temperature of 930° to 1020° F. If part of the ash fuses over the unashed carbonized material, it is almost impossible to remove all of the carbon. Ashing should therefore be at as low a temperature as possible, preferably below 930° F.

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Water-insoluble matter. — This determination, suggested by L. H. Blood, a chemist with the J. Howard Smith Co., Port Monmouth, N. J., was found to be of considerable value and accordingly was used in the analysis of all the 1953 season series of samples of condensed solubles.

A 10-g. sample is weighed into a tared 100-ml. beaker. Exactly 0.500 g. of ignited infusorial-earth filter aid and 75 to 80 ml. of boiling distilled water are then added. The mixture is stirred to thoroughly dissolve and disperse the solubles and filter aid. Then the suspension is filtered with suction through a weighed 9.0-cm. No. 40 Whatman paper on a Buchner funnel. The filter paper is predried at 215° F. in an air oven and weighed immediately on removal from the oven, because the paper picks up moisture very quickly. The filter-aid suspension usually filters quite rapidly, and the contents of the beaker are washed quantitatively into the funnel with hot water from a wash bottle. The material on the paper is washed several more times with hot water, then several times with 95-percent ethyl alcohol, and finally several times with ether. In this way, oil as well as water-soluble material is removed. The paper is carefully removed from the funnel with the thin cake intact, dried for half an hour in an air oven at 215° F., and weighed immediately. The figure thus obtained, minus the filter-paper tare weight and the 0.500 g. added filter aid, is the weight of insoluble matter.

Water-insoluble ash.—It has been generally assumed that most of the insoluble material in solubles was the "mud" often mentioned by plant personnel as being present in the fish and in the condensed solubles from certain areas or at certain times of the year. This very finely divided sludge, or "mud," was thought to be largely inorganic material. To determine the validity of the premise, the water-insoluble solids from the solubles were ashed. The weight of ashed material must, of course, be corrected for the added filter aid by subtracting 0.500 g. Only one sample had enough insoluble ash to substantiate the belief that the mud was composed of inorganic material.

Four physical constants are considered to be of importance in defining and differentiating condensed solubles. These are listed below and are accompanied by a short explanation of their significance to the industry.

pH.—The pH is usually checked at the plant, and an attempt is made to adjust it to a definite value by the addition of sulfuric acid to the finished solubles. In this process the added acid serves primarily as a preservative. Measurements of pH give an indication of the degree of plant control that has been maintained and permit a check on the possibility that a change in pH occurs during prolonged storage.

Refractive index.—The refractive index is of interest because of the quite general use throughout the industry of a small hand refractometer for estimating the total solids during a run. For most plants, this instrument is the only means, other than subjective observations based on the experience of

the operator, of determining when the desired concentration of solids has been reached. The instrument has an engraved scale on the glass endplate which reads directly in percent solids. However, information obtained from the manufacturer does not indicate that the scale was calibrated against this type of material, and the basal calibration curve of refractive index to percent solids was not available. For the purpose of this investigation, interest centered on the correlation between the total solids and the actual refractive index as determined with a Bausch and Lomb refractometer.

Specific gravity.—The determination of specific gravity is the second method that is practical for plant use to indicate when a batch of solubles has reached the desired concentration of 50-percent solids. For specific gravity, as well as for refractive index, the object was to determine how close a correlation existed between these two variables. In the laboratory, specific gravity was determined with an aluminum pycnometer specially designed for semifluid materials, such as tars or asphalt (Fisher Scientific Co., Pittsburgh 19, Pa., No. 3–427). The chief difficulty encountered was to obtain a properly mixed sample for the determination without entrapping air in the mixture. Small air bubbles, once mixed into the more viscous samples, are very slow to separate and can lead to considerable error in the results.

Viscosity.—The viscosity of condensed menhaden solubles showed the greatest range of any of the variable factors studied and was at the same time a property for which controlled uniformity would have considerable practical significance. There are numerous means of measuring viscosity, some of them suitable for only limited ranges. A MacMichael viscosimeter, which was available in the laboratory, proved to be reasonably satisfactory for most of the samples. Measurements were made at room temperatures of 78° to 85° F. The principle of this instrument is based on the measurement of the angular motion, or "pull," imparted to a bob. The viscous fluid in which the bob is suspended is held in a cup on a turntable that is rotated at a constant speed. The bronze suspension wire, suitably calibrated, also carries a dial calibrated in degrees, which makes it possible to measure the angular rotation of the bob at the point at which it is balanced by the torsional stress in the bronze wire. By changing the wire, a very large range of viscosities can be measured, and for extremely high viscosities a smaller bob may be substituted.

Chemical and physical data for condensed solubles

The data for the 11 characteristics for the individual samples are presented in table 1. The 32 samples that were collected include some obtained directly from the evaporators, but most of the samples were taken from storage tanks. Samples are further identified by the month and year of the sample collection, the general geographical origin, and code numbers indicating different plants within each area. The North Atlantic designation includes States

north of Chesapeake Bay; the south Atlantic includes Chesapeake Bay south to Florida; the East Gulf covers the area east of the Mississippi Delta; and the West Gulf covers the area west of the delta.

In addition to the analytical data, the composite rating of the general suitability of the condensed solubles for the preparation of dried solubles is included. The method of deriving the Suitability Factor is described in an earlier section.

The primary object of the investigation was to prepare satisfactory dried solubles from condensed solubles. It developed, however, that condensed solubles were so variable that it was virtually impossible to make an unqualified statement about the dried product that would be obtained from this raw material. If condensed solubles were to be used for this purpose, it seemed essential to obtain a more definite correlation of the characteristics of the raw material to desirable properties of the dried product.

Suitability Factor scattergrams

The drying behavior and properties of the dry products had been rated, and these ratings had been combined, as described in a preceding section, to give a single value called the Suitability Factor. It was thought that these values, when plotted as abscissa with the data for 10 of the chemical and physical characteristics for the 32 samples of condensed solubles as ordinates, might yield the desired information. To facilitate comparison of the 10 resulting scattergrams, the ordinate scales were selected so that the total observed ranges covered approximately the same distance on the Y-axis for each variable.

The resulting scattergrams are reproduced in figures 3 to 12. The original graphs were drawn on translucent plastic sheets to make it possible to note similarities in distribution of any two or more sets of data by placing the graphs one over the other with axes coinciding. This procedure also facilitates the selection of sets of data for the calculation of simple and multiple correlations. The individual scattergrams permit a quick estimate of the degree of correlation of any given characteristic to the Suitability Factor. In other words, they permit one to judge the value of a given characteristic as a criterion for selection of condensed solubles that are most likely to produce a desirable dry product.

Inspection of the scattergrams (figs. 3 to 12) shows that none of the variables has a sufficiently high degree of correlation with the Suitability Factor to justify its selection as a single criterion of choice. A positive correlation would manifest itself in a concentration of charted points along a line from the lower left-hand corner to the upper right-hand corner of the graph, whereas for a negative correlation, points would be distributed from upper left to lower right. Although none of the characteristics shows marked correlation to Suitability Factor, several (free ammonia, total ash, pH, and specific gravity) show some degree of positive correlation, while an inverse relation is indicated for water-insoluble matter and for viscosity. Inspection of data indicates

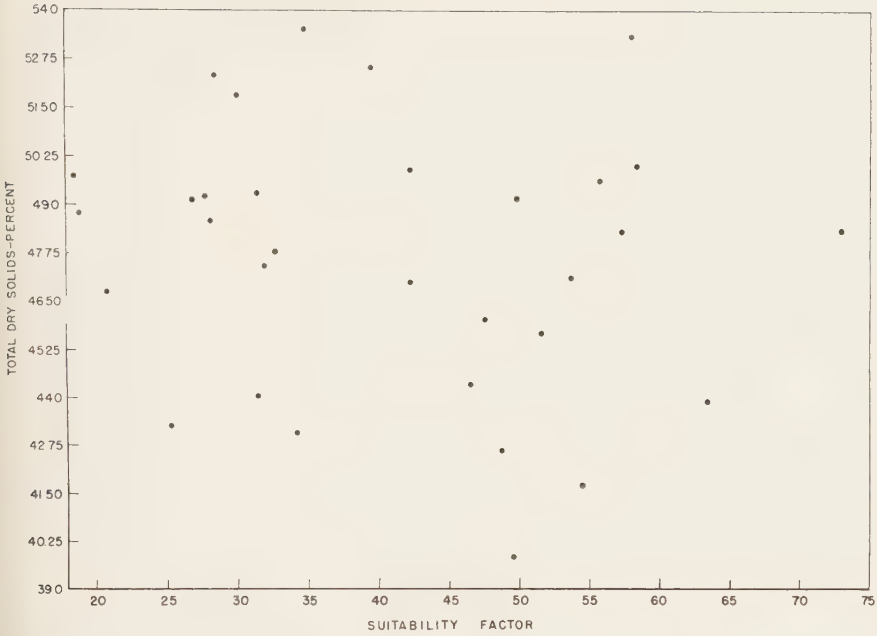

Figure 3.—Correlation of percent of total dry solids in condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

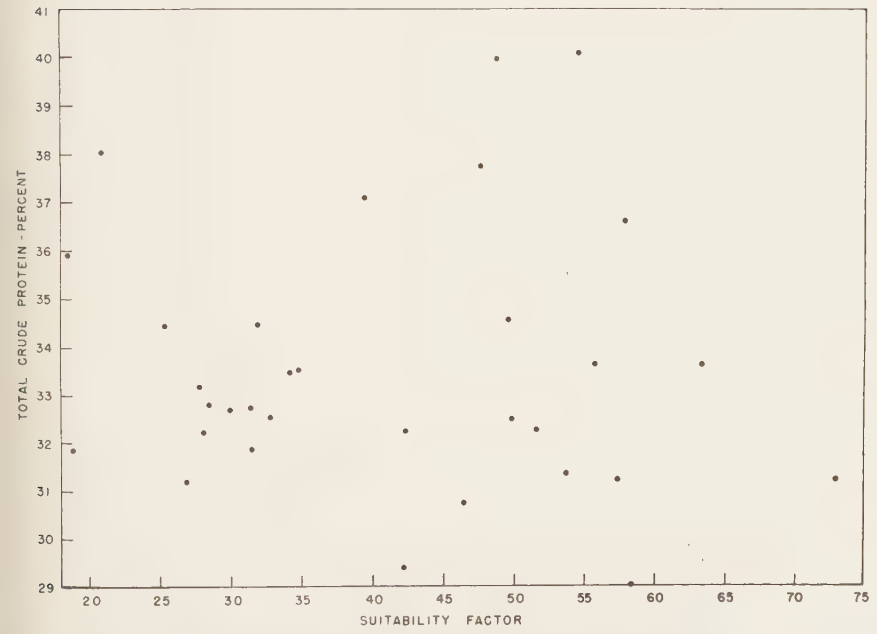

Figure 4.—Correlation of percent of crude protein in condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

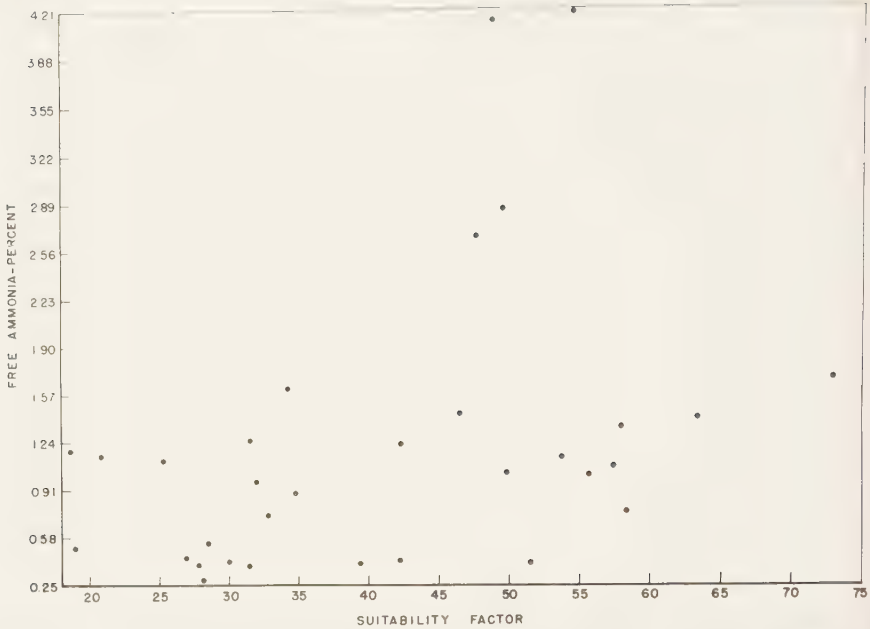

Figure 5.—Correlation of percent of free ammonia in condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

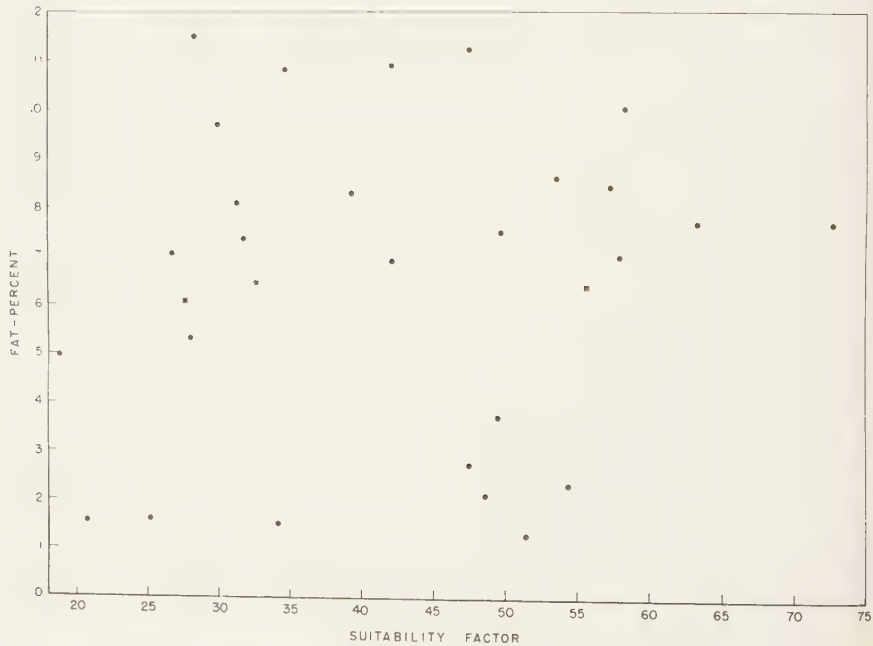

Figure 6.—Correlation of percent of fat in condensed menhaden solubles and Suitability Factc of corresponding drum-dried product.

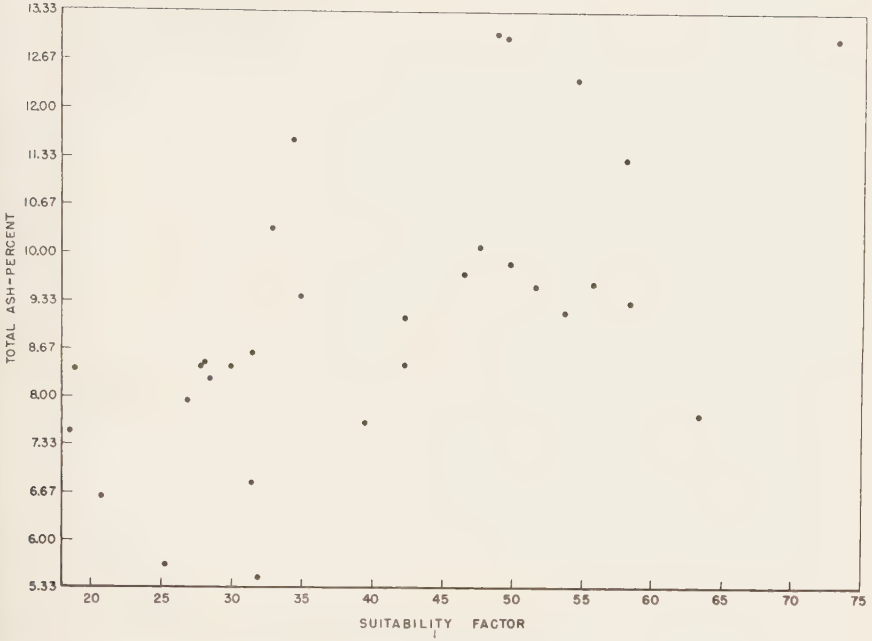

Figure 7.—Correlation of percent of total ash in condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

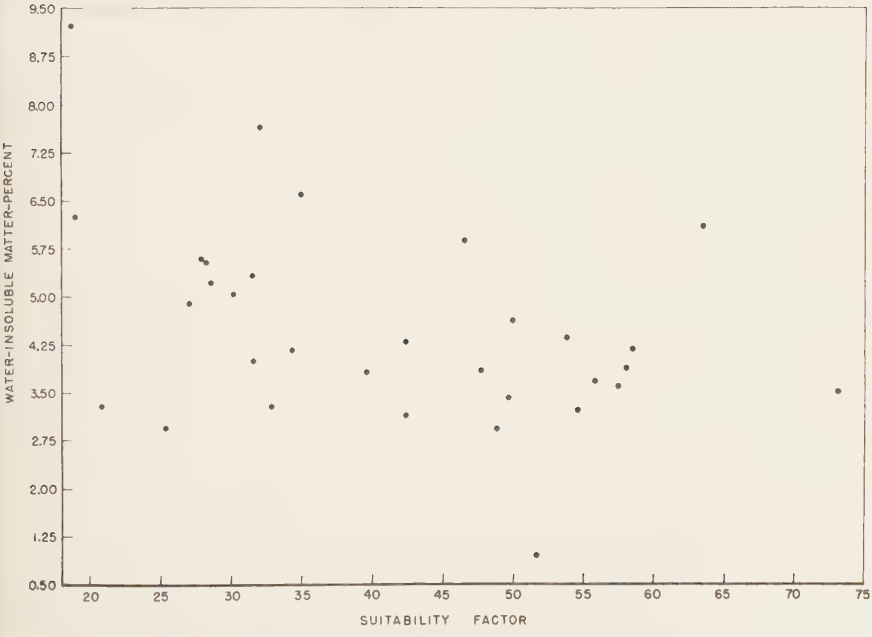

Figure 8.—Correlation of percent of water insoluble matter in condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

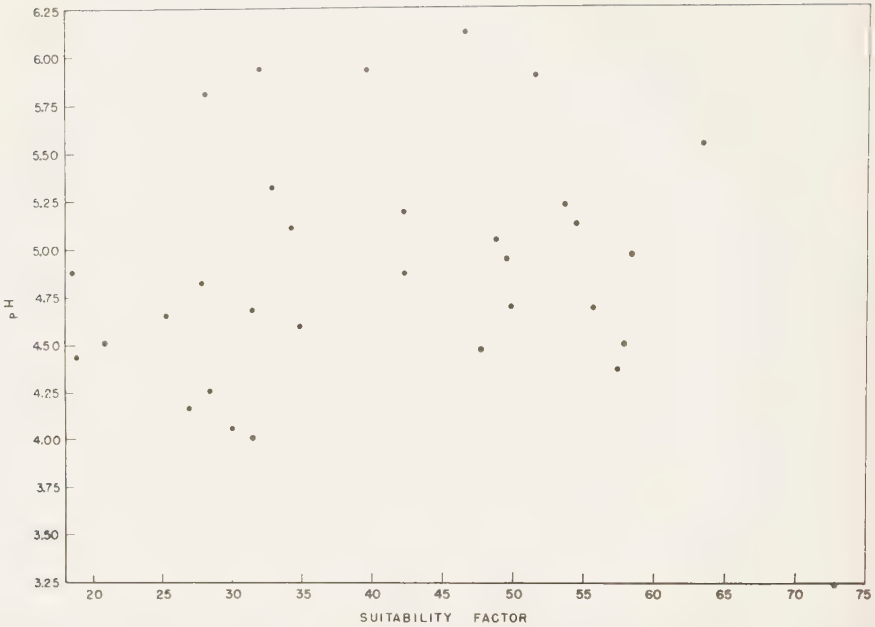

Figure 9.—Correlation of pH of condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

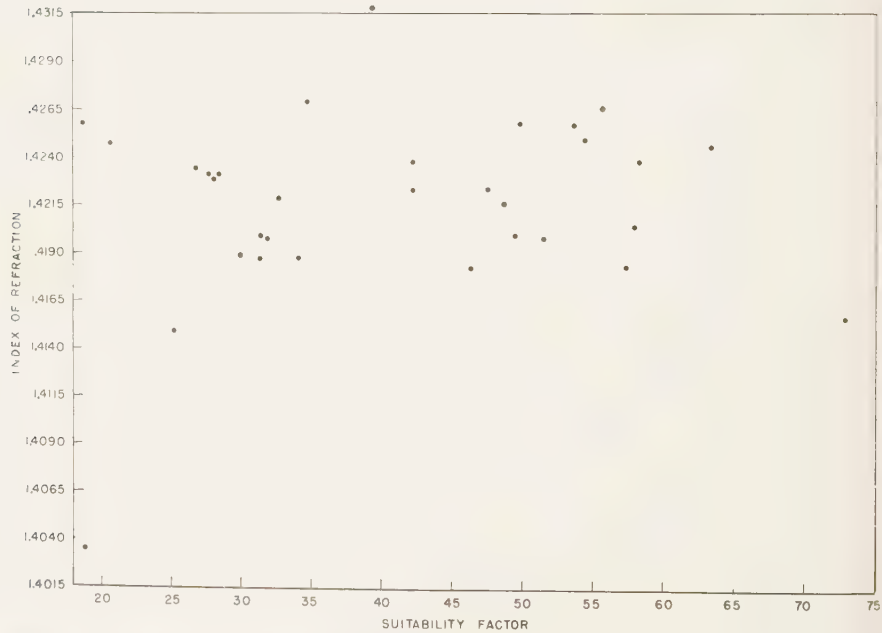

Figure 10.—Correlation of index of refraction of condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

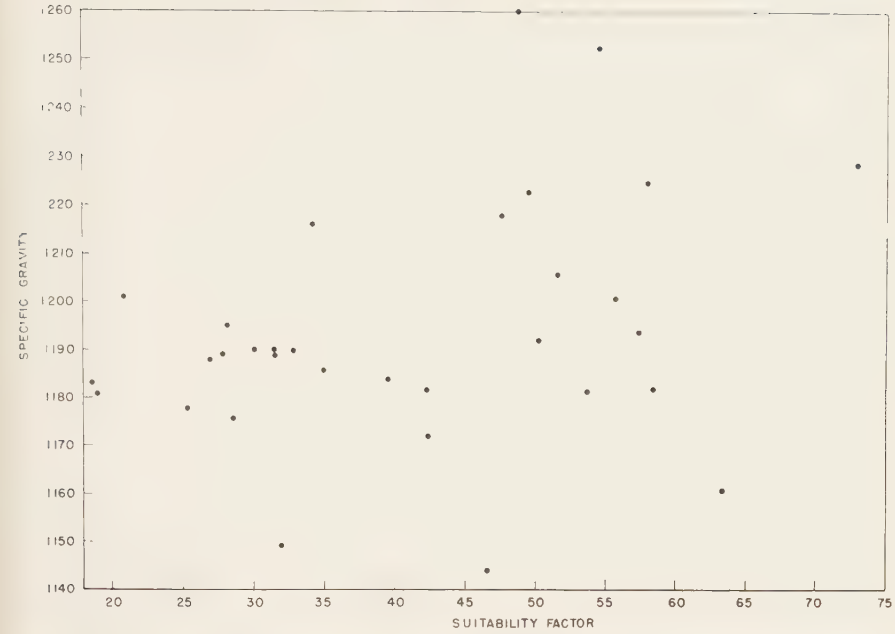

Figure 11.—Correlation of specific gravity of condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

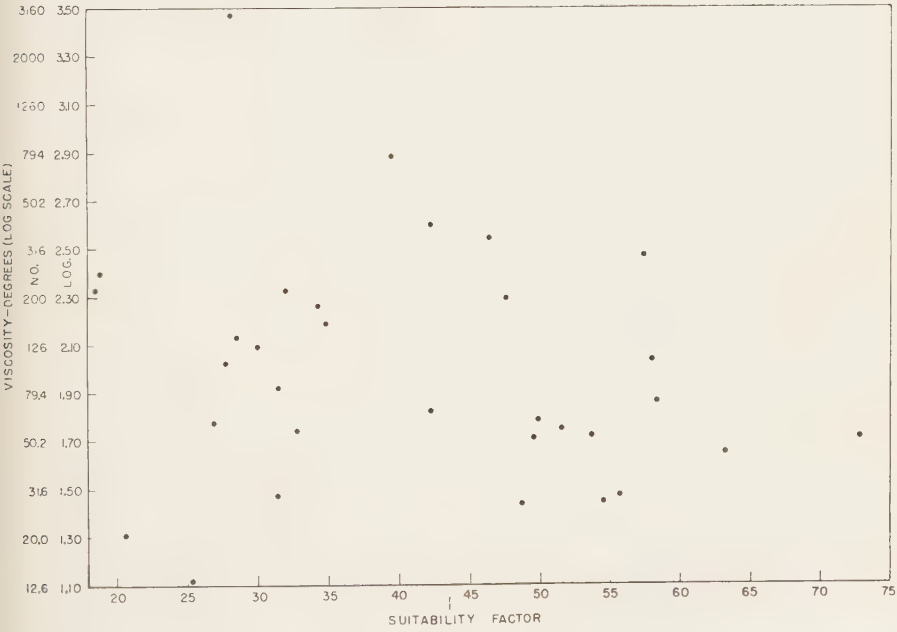

Figure 12.—Correlation of relative viscosity of condensed menhaden solubles and Suitability Factor of corresponding drum-dried product.

little or no correlation of the content of the total solids, protein, and fat, or of the index of refraction to suitability of condensed solubles for making a satisfactory dry product.

It is planned eventually to determine the correlation coefficient of each of the characteristics to the Suitability Factor, and to determine multiple correlations wherever data indicate some interaction. In addition, the degree of intercorrelation of values will be tested for data groups, such as specific gravity and refractive index to total dry solids, as well as for some other suspected relations, such as high viscosity to high oil content, and high ammonia content to low viscosity. It is planned to release the results of these statistical analyses as a supplementary section to this more generalized report.

Some difficulty in obtaining the desired degree of correlation of characteristics of the condensed solubles to the Suitability Factor would be expected, owing to the composite nature of the latter. In some instances, single characteristics do appear to show a somewhat greater correlation to other variables. Observation of this group of samples indicates, for example, that high viscosity is sometimes associated with high oil content and oil separation during drying, whereas very low viscosity is associated with low oil content and dustiness of the dry material. Dry solubles with high oil content are darker than those with low oil content. Solubles samples with high ammonia content usually gave off more unpleasant odors when heated on the drums. Since the pH of the nonacidulated samples was on the acid side of neutral (maximum pH 6.13), any ammonia present would be in the form of an organic amine, or would be combined with the added sulfuric acid. The unpleasant odors associated with the high ammonia content were probably due to the most part to volatile amines or other simple nitrogenous derivatives formed during the autolytic spoilage of the stickwater before evaporation. There also appeared to be a direct association between a high level of ammonia in the solubles and high moisture absorption in the humidity chambers. However, there are exceptions for every such generalization, and a statistical analysis will be necessary before it will be possible to determine the relative significance of these or other apparently related factors.

Dry solids versus refractive index and specific gravity

One of the rather surprising conclusions that might be drawn from these data is that neither the refractive index nor the specific gravity is a particularly accurate indicator of the total solids content of condensed solubles. Figure 13, showing these variables plotted against dry solids, illustrates graphically this lack of close correlation. This lack of a quick and accurate method of determination of solid content undoubtedly accounts for the observed range in dry solids from 39.8 to 53.5 percent, median 48.4 percent. Every effort is made to manufacture a product with 50-percent solids, but this is sometimes difficult to attain with present check equipment

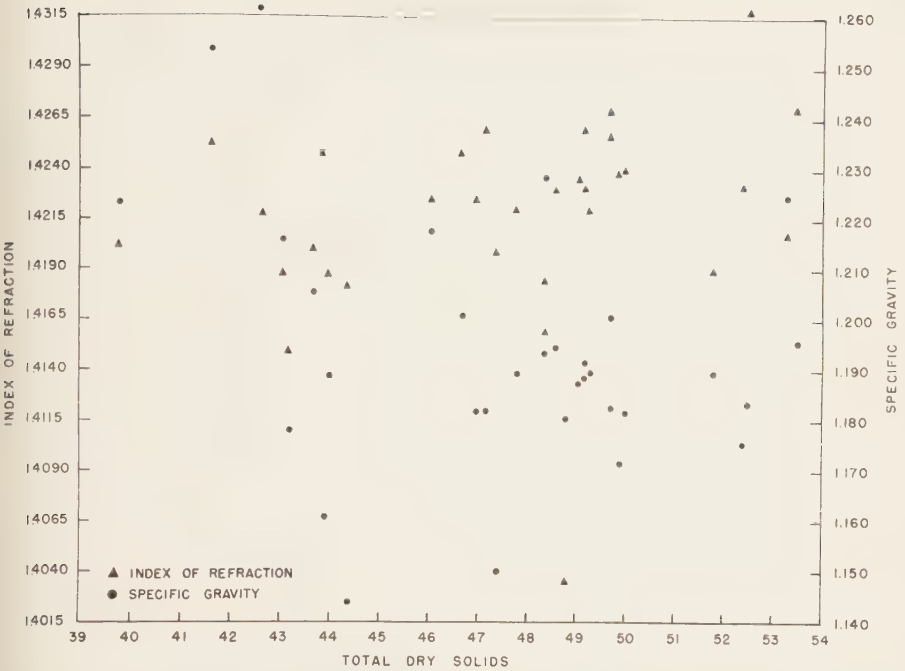

Figure 13.—Correlation of index of refraction and of specific gravity and percent of total dry solids for 32 commercial samples of condensed menhaden solubles.

Crude protein and corrected protein

The crude protein showed less variation than might be expected from the dry-matter data. Some of the high protein values, however, were due to excessive ammonia. A column in table 1 gives the content of protein corrected by subtracting the protein equivalent of the ammonia nitrogen.

Crude protein, in general, amounted to the expected level of 32 to 33 percent (median 32.7), but the data from several feeding tests have shown that condensed fish solubles, although serving as an excellent supplement or complement when used with fish meal, do not supply all the necessary amino acids when used alone.

Ammonia

All of the samples showed the presence of some ammonia, herein defined as the nitrogenous substances volatile with an excess of calcium hydroxide. The amount varied from a low of 0.28 percent to a high of 4.19 percent ammonia, or a range of about 15 times the low value. There are excellent indications (chiefly the odor) that the amount of ammonia is closely associated with the freshness of the original raw fish and with the speed with which the stickwater is handled from press to evaporators.

Fat

The fat, or oil content, of menhaden solubles showed unusually large variation, considering that

this factor is under plant control. The amount of oil remaining in the solubles is determined by the efficiency of the oil separation, whether by centrifuge or by settling system. The oil is worth more when separated than when sold as part of the solubles—about twice as much during the 1955 season. Plant operators therefore would like to reduce the oil content of solubles to not more than 5 percent. That this goal is difficult to attain in usual plant practice is evident from the data, which show that only 10 of 33 samples contained less than 5 percent oil. Of these 10 samples, half were also the samples with the highest free-ammonia value, for which low oil has been obtained at the expense of protein loss through excessive autolysis. In these cases, viscosity is also reduced, as well as the emulsifying capacity of the solubles, so that little oil is held in suspension.

Total ash

Total ash showed a much larger variation than would be expected, since it is not the practice of the menhaden industry to use salt or any other inorganic preservative for the raw fish. The maximum value was some 2½ times the minimum, and the values were scattered fairly evenly within this range. No reason for this variability is known, and its significance is difficult to interpret. Indications are that the inorganic consituents of condensed solubles are inert chemically but exert considerable influence on other properties of the solubles.

Water-insoluble matter

The data on water-insoluble matter were of interest from several points of view. Values were unexpectedly low and constant, in view of the general impression that solubles contain considerable quantities of finely divided organic solids and inorganic muds. With the exception of one low and two high values, the data had a range of 3.0 to 6.8 percent. It was rather unexpected to find that this insoluble material was predominantly organic matter. The insoluble ash content of the typical sample was only about 5 percent of the insoluble matter, or 0.22 percent of the original solubles.

Water-insoluble ash

Water-insoluble ash content was so low, with only two values exceeding 0.57 percent, that it may be assumed that true "mud"—that is, colloidal silicates—is unimportant as a source of contamination or dilution of solubles.

pH

Sulfuric acid is used by the menhaden industry primarily as a preservative and usually is added at some place in the system between the evaporators and the storage tanks, or it may be added in the latter. In either case, thorough mixing of the relatively small volume of acid into a large tank of solubles is difficult and slow, because agitation normally is accomplished by means of an external circulating pump. This difficulty in obtaining thorough mixing no doubt accounts, in part, for the range of pH values from 3.28 to 5.58 for these samples. Most producers attempt to obtain a pH of about 4.5 for the finished solubles, which is quite

close to the observed median of 4.69. Six of the samples were taken before the acid was added, but even these samples had pH values slightly on the acid side, averaging 5.92.

Several men in the industry have stated that they believe the pH increases during storage. Of 23 samples that had been stored for 17 months in a refrigerator, 2 had no change in pH, 13 had insignificant increases of 0.02 to 0.08 units, 3 had somewhat larger increases of 0.13, 0.15, and 0.23 units, and 5 had decreases of 0.04 to 0.11 pH units. Most of these changes are probably within the limit for error of measurement, but the three largest may be significant. Greater changes would be expected at higher temperatures, therefore the present data are inconclusive in regard to possible increases that might occur under normal commercial storage conditions.

Specific gravity

Specific gravity of condensed solubles would appear to be affected by two variables in addition to total dry solids. High oil content has the effect of reducing the specific gravity, whereas high total ash content tends to increase this value. A multiple-correlation study of these four variables will be reported in a later paper.

Viscosity and thixotropy

Viscosity, as previously indicated, showed the greatest variation of any of the physical or chemical characteristics studied. The maximum value was more than 200 times the minimum. Physically, this range extended from an almost water-thin liquid to a rather rubbery semisolid that had to be warmed up to about 105° F. before it could be poured from the container. Further study would be needed to permit even a preliminary understanding of the various factors affecting viscosity. Some of them—such as age or subspecies of fish, and local air and water temperatures—are beyond the processor's control. Others—such as condition of fish on landing, time in the raw box, and time from presses to evaporators—were not subject to measurement or control in this study. Some of these latter factors might be controllable, if it were found to be important to do so.

An interesting characteristic was noted during measurement of viscosity with the MacMichael viscosimeter. Most of the samples reached a constant dial reading within a few seconds after the turntable motor was started. About six samples, however, showed a definite drop in the apparent viscosity, with the dial reading gradually decreasing for several minutes to a more stable lower value. This drop in viscosity with disturbance or agitation of the solution is known as thixotropy and is usually associated with flocculent suspensions of very fine solids. The peculiar behavior of some condensed solubles was not limited to this phenomenon. Five samples showed some degree of negative thixotropy, that is, the viscosity *increased* with agitation over a period of time. For two samples this increase was quite marked. Apparently, negative thixotropy is a rather rare phenomenon, because we could not find much information

in the available references on physical chemistry. Neither positive nor negative thixotropy appeared to be associated with any particular level of viscosity, as the dial readings were in the upper middle range of 106° to 255°. The samples showing thixotropy, and a rough indication of its extent (1 to 4 plus or minus), are noted adjacent to the viscosity value in table 1.

The overall range in viscosity o all samples was 13° to 3,000°, wit a median value of 78°. Reading were as nearly as possible the initia value, but they were somewhat dif ficult to obtain accurately for th thixotropic samples because no defi nite point of equilibrium wa reached.

EFFECTS OF ADDITIVES ON PROPERTIES OF DRY SOLUBLES

The third and final phase of this investigation involved the preparation of mixtures of condensed solubles with additives, the determination of the drying behavior of these mixtures, and the determination of the properties of the dry products.

As was mentioned in a preceding section, solubles have been mixed with a number of different carriers to give dry products of more desirable characteristics, particularly as regards hygroscopicity. Most of these mixtures are believed to have contained relatively small amounts of solubles solids, although the formulas are not usually made known to the public. This investigation was limited to the use of only small amounts of additives so that solubles solids constituted 75 percent or more of the dry product.

Three types of additives were tried, using, as the carrier, solubles that had presented difficulty of one kind or another in preparing the pure dry product. Some of these pure dried solubles were excessively oily, whereas others showed an undesirable level of hot plasticity, roll adherence, hygroscopicity, or odor. Two general types of additives were used: those that were chemically active, and those that were chemically inert. The latter type was further divided into nutritionally inert additives and those with food value

Chemically active additives

The first additive tried was calcium hydroxide (slaked lime) since it was considered possible that the hygroscopic nature of the dry solubles might be due to the presence of sulfuric acid or various sulfate salts. An excess of the dry powder was mixed in the soluble with a spatula, and the mixture was dried. Addition of calcium hydroxide resulted in the liberation of ammonia and the formation of an extremely thixotropic mixture. The calcium salts apparently crystallized in the same manner as in the setting of plaster of paris, but there was enough water present so that the crystal structure was easily broken up by stirring the mixture.

The solubles–calcium salts mixtures were easier to dry and grind than the corresponding pure solu

bles, being less hot- and cold-plastic. There was little additional benefit from the additive, because these mixtures were slightly more hygroscopic than the pure solubles. This trial with calcium hydroxide was made before the development of the numerical rating system, so a direct comparison of the product made with and the product made without this particular additive was not made.

The following season, 1953, after the regular series of pure dried solubles had been completed, two additional series with various additives were studied. As before, condensed solubles samples were selected from those that, for various reasons, had been difficult to dry.

In the first series, several more chemically active additives were tried. Since the calcium hydroxide had led to a loss in ammonia and a reduction in apparent (crude) protein, aqueous ammonia (30 percent) was used to neutralize the sulfuric acid in one group of samples. The ammonia was added in small increments to eight samples of solubles. A Waring blender was used to thoroughly mix these ingredients, and the pH was checked after each addition. For six of the eight mixtures the final pH was approximately the neutral point, 6.93 to 7.51, but the pH of one sample was 7.90, and that of another sample was 9.20 (table 4).

Four of these eight solubles samples were also neutralized with fairly concentrated solutions of potassium or sodium hydroxide. Those treated with potassium hydroxide were made slightly alkaline to final pH values of 7.0 to 8.2. Sodium hydroxide was added to the second group to give pH values of 9.1 to 10.1.

The data for this series are summarized in table 4. It is evident that ammonia and sodium hydroxide, as additives, can offer little benefit in preparation of dry solubles. The Suitability Factor values were higher for six of the eight mixtures with ammonia and for two of the four mixtures with sodium hydroxide. Potassium hydroxide was the only base that produced consistent improvement. Most of the improved score was derived from reduced hot- and cold-plasticity and less oil separation. This latter condition resulted from the formation of sodium and potassium soaps through the reaction of the alkalies with the free fatty acids in the oil.

The dried solubles made with ammonia and sodium hydroxide as additives showed quite a marked increase in moisture absorption in humidity chambers. In fact, the initially selected interval range, based on this characteristic for the pure dried solubles, did not cover the observed range for the additive lots and had to be extended. One mixture had a rating of 18, and another had a score of 26 on the extended scale. The maximum rating for pure dried solubles had been 10.

Chemically inert additives

Since none of the chemically active additives showed sufficient promise to justify the expense, not to mention the difficulty and potential danger in working with these chemicals in a menhaden plant,

Table 4.—Characteristics of dried menhaden solubles prepared with several alkaline additives

Sample description	pH	Oil separation [1]	Plasticity [1]		Color [1]		Drum adherence [1]	Homogeneity [1]	Vapor odor [1]	Moisture absorption in humidity chambers [1]	Texture after humidity test [1]	Suitability Factor	Change [2]
			Hot	Cold	Original	Ground							
												Percent	*Percent*
No. 151a:													
Pure solubles	5.58	30	56	16	18	18	2	6	42	32	49	63.6	
Plus ammonium hydroxide	7.40	35	49	28	18	16	2	4	36	44	49	66.9	+5.2
No. 152a:													
Pure solubles	4.52	5	63	32	16	12	2	1	36	24	56	57.5	
Plus ammonium hydroxide	7.52	10	63	32	18	12	2	1	24	40	63	62.5	+8.6
No. 153a:													
Plus solubles	3.24	25	56	28	16	16	2	3	54	32	70	72.8	
Plus ammonium hydroxide	7.51	25	42	32	18	16	2	1	42	36	70	67.8	−6.8
Plus potassium hydroxide	7.02	10	21	20	20	18	2	1	42	36	63	53.6	−26.3
Plus sodium hydroxide	9.10	5	21	16	18	16	2	1	36	72	70	60.3	−17.2
No. 158a:													
Pure solubles	5.14	5	56	36	12	4	2	3	42	20	56	54.4	
Plus ammonium hydroxide	7.90	5	42	32	6	4	2	2	54	32	56	54.2	−0.4
Plus potassium hydroxide	8.10	5	28	28	6	6	2	1	24	8	56	34.4	−36.8
Plus sodium hydroxide	9.20	5	28	24	6	6	2	3	48	24	63	46.9	−13.8
No. 165a:													
Pure solubles	5.10	5	49	12	14	8	2	6	42	24	49	47.5	
Plus ammonium hydroxide	6.93	5	56	24	12	6	2	5	42	28	63	56.4	+18.7
Plus potassium hydroxide	8.20	5	42	16	8	8	2	3	24	24	56	41.1	−13.5
Plus sodium hydroxide	9.32	5	42	12	18	8	2	5	36	80	70	66.1	+39.2
No. 168a:													
Pure solubles	5.12	5	28	8	4	2	2	1	24	40	49	34.2	
Plus ammonium hydroxide	7.02	5	42	16	2	2	2	1	24	72	63	52.5	+53.5
No. 174a:													
Pure solubles	4.39	25	42	12	16	14	2	3	48	28	56	57.2	
Plus ammonium hydroxide	7.25	15	56	24	18	16	2	1	54	44	63	70.3	+22.9
Plus potassium hydroxide	7.71	15	28	12	14	16	2	1	42	32	56	49.4	−13.6
Plus sodium hydroxide	10.10	5	14	12	12	16	2	1	48	104	63	65.8	+15.0
No. 176a:													
Pure solubles	5.81	5	21	4	10	10	20	4	66	40	21	28.1	
Plus ammonium hydroxide	9.20	5	14	4	8	12	40	6	12	60	28	41.4	+47.3

[1] The values are the product of "weight" times "rating", as described in the footnotes of table 3 in calculation of the Suitability Factor.
[2] These values represent the plus or minus change in the Suitability Factor due to the additive expressed as percent of the original.

three inert additives were tried with another group of difficult-to-dry solubles. A fish meal was chosen as one additive because of its availability and nutritive value. Two inert absorbent powders were also tried. One was a light fluffy cellulose material (trade name "Polycel"), and the other was a very fine (325-mesh) silica gel.

The fish meal was reground and mixed into the condensed solubles in a blendor at the rate of 5 or 10 percent by weight of the solubles, or approximately 10 and 20 percent of the solids in the dry product. The coarser material in the menhaden meal floated to the surface when mixed with the solubles, therefore two additional mixtures with 10-percent fish meal were prepared with the "fines", which passed through a 20-mesh sieve.

The silica gel was tried at a 3-percent level with two samples. Supposedly, this level is effective in controlling hygroscopicity in other products. When it became obvious that this amount of silica gel produced little improvement, one mixture with 10 percent silica gel was tried. Polycel was tried at the 2.5- and 4.0-percent levels by weight. The latter amount was almost the maximum possible, because the Polycel was so light and bulky that the addition of 4 percent resulted in a thick, rather pasty mixture.

These data are summarized in table 5. The moisture-absorption ratings are not included, because the humidity chambers had been dismantled before this series was run. However, two samples with low-oil content, which originally had been so hygroscopic that they could hardly be ground, were equally troublesome with either fish-meal or silica-gel additives. Odor appeared to be accentuated in some cases, and the samples were less homogeneous. Otherwise, most of the scores showed some improvement, as would be expected with any inert

Table 5.—Characteristics of dried menhaden solubles prepared with inert additives

Sample description	Additive proportion by weight	Oil separation [1]	Plasticity [1]		Color [1]	Drum adherence [1]	Homogeneity [1]	Vapor odor [1]	Partial suitability factor [2]
			Hot	Cold					
No. 154a:									*Percent*
Pure solubles		20	21	8	6	10	1	6	18.5
Plus fish meal	1 to 9	10	28	8	14	16	7	30	35.4
Do	1 to 19	15	42	12	12	18	6	30	44.4
No. 156a:									
Pure solubles		35	28	16	12	2	1	12	32.5
Plus fish meal (20-mesh size)	1 to 9	30	49	16	16	2	7	36	53.1
Plus Polycel	1 to 38	25	28	8	12	2	2	30	32.9
Do	1 to 24	15	14	8	8	2	7	24	21.0
No. 158a:									
Pure solubles		5	56	36	12	2	3	42	53.1
Plus silica gel	1 to 33	5	56	36	6	2	1	42	49.8
Plus fish meal	1 to 9	5	35	28	14	2	8	30	39.1
No. 165a:									
Pure solubles		5	49	12	14	2	6	42	42.4
Plus silica gel	1 to 33	5	35	28	12	2	4	24	34.2
Plus fish meal	1 to 19	5	42	24	16	2	8	24	38.7
No. 175a:									
Pure solubles		25	49	12	14	6	1	12	37.9
Plus silica gel	1 to 9	20	14	4	10	8	1	16	18.9
Plus fish meal (20-mesh size)	1 to 9	40	42	12	16	18	5	16	50.2

[1] The values are the product of "weight" times "rating," as described in the footnotes of table 3 in calculation of the Suitability Factor.

[2] These values are not directly comparable with those in table 1, because they do not include data related to moisture absorbed in the humidity chambers.

nonhygroscopic diluent. However, there was not a single case where improvement was marked enough to warrant the supposition that any of these additives, in the proportions used, was an unfailing cure for any of the undesirable drying, grinding, and storage characteristics encountered with these more-difficult-to-dry solubles.

Storage characteristics

In the final analysis, the decision whether any given lot of experimentally dried solubles might have future commercial possibilities would depend on the storage characteristics of the dry product. These are, unfortunately, quite difficult to determine, since they cannot be related with certainty to any physical or chemical variables that can be determined in the laboratory. In this investigation an attempt was made to determine storage characteristics in the laboratory of all lots of dry solubles that had not already caked in the screw-top bottles used to hold the ground samples, by packaging small amounts (100 to 150 grams) in specially made small bags of three-ply asphalt and kraft paper. The open end of each bag was heat-sealed and folded twice, and the fold was again heated and crimped in the sealer. These bags were weighed and then exposed from late June to September to summer humidities common in the laboratory in College Park, Md. In spite of the protective bag, all of the 15 samples of dry solubles picked up moisture slowly but steadily—the gain in weight ranged from 5.0 to 7.6 percent. The bags were weighed again in January, when room humidity was low, and were found to have lost 2 to 3 percent in weight.

When the bags were opened, only one sample of packaged dry solubles was crumbly and free flowing. One sample was quite oily and loose textured, 7 had caked fairly hard and dry, and 6 were no longer dry but were more or less soft-plastic, that is, the particles were adhering. One of the samples contained sufficient oil to soak through the bag paper, partially dissolving the asphalt so that the outside had a black sticky surface. Two others showed some oil penetration to the exterior. It was felt that the results of this trial augured little success for packaging dry solubles, even in bags that are normally moisture resistant. On the other hand, it was considered possible that in a 100-pound bag caking might have been limited to a fairly thin shell under the paper. This shell might retard further moisture penetration and give much more satisfactory results.

It was not possible to duplicate these conditions in the laboratory, so the storage test was not repeated. It has been demonstrated in this trial, however, that the moisture-absorptive properties of dry menhaden solubles would be one of the major problems in the commercial production and distribution of the pure product. Packaging in bags made of polyethylene, or some similar completely moistureproof plastic film, would be needed to control this characteristic.

SUMMARY

Although the dried solubles samples prepared by drum drying in this laboratory showed considerable variation in their rating of moisture absorption in humidity chambers, even the best in this respect was more hygroscopic than fish meal and could not be stored in the atmospheric condition normal to coastal areas during the production season without some type of protective packaging. Moreover, the additives used, in proportions of less than one-fourth of the total dry solids, did not radically improve this undesirable characteristic.

Perhaps two-fifths of all the samples of menhaden solubles tested in the present series dried readily and gave a dried product that was only moderately hygroscopic. Several additives were tried with selected samples of the other more-difficult-to-dry samples to determine whether they would improve the undesirable characteristics of the pure dried product. Chemically active additives, such as calcium, ammonium, sodium, and potassium hydroxides, generally resulted in less oil separation during drying and in reduced hot-plasticity, but these additives did not improve the hygroscopic nature of the dry products. The inert additives tried (a fish meal, a specially prepared cellulose, and a finely divided silica gel) were mixed into the condensed solubles at levels of 10 percent or less. These additives produced mixtures with moderately improved drying characteristics.

CONCLUSION

The preparation of a dry product by drum-drying random lots of condensed menhaden solubles cannot be recommended as a routine operation because of the inherent variability in the raw material. The factors causing this variability are only partially understood. Therefore, no recommendations can be made at the present time for modification of the handling and processing of condensed solubles to yield a product suitable for this purpose. None of the additives were effective in overcoming undesirable characteristics.

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